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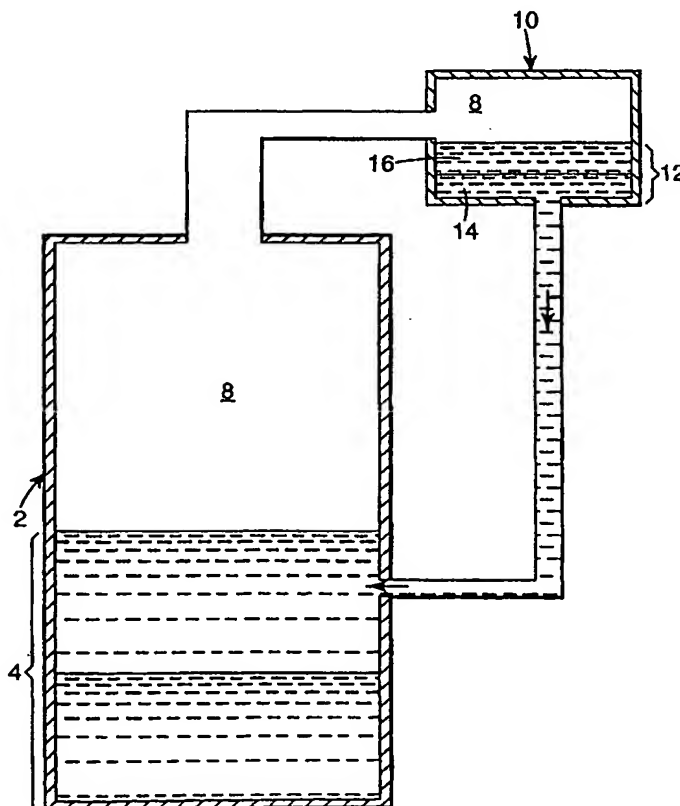
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<b>(21) International Application Number:</b> PCT/US98/27777 <b>(22) International Filing Date:</b> 29 December 1998 (29.12.98) <b>(71) Applicant (for all designated States except US):</b> MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only):</b> BOYD, Steven, D. [US/US]; 6921 Macbeth Court, Woodbury, MN 55125 (US). <b>(74) Agents:</b> SCHULTE, Daniel, C. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** DEHYDRATION PROCESS**(57) Abstract**

Described are methods for dehydrating a hydrous substrate by combining the hydrous substrate with a hydrofluorocarbon, such as a hydrofluoroether. The process can include the step of removing water from the combined substrate and hydrofluoroether composition, e.g., by volatilization.



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## DEHYDRATION PROCESS

### Field of the Invention

This invention relates to a process for removing water from hydrous  
5 substrates.

### Background

Many materials, including chemical materials and compositions, and articles  
of manufacture, are water-sensitive or for other reasons are desirably free or  
10 substantially free of water. Examples of chemicals used in water-sensitive chemical  
systems include surfactants such as fluorinated surfactants, urethanes,  
pharmaceutical compounds, and many chemicals and chemical systems useful in  
energy storage systems and devices (e.g., batteries, capacitors, etc.).

Some of these and other chemicals used in water-sensitive chemical systems  
15 may be manufactured in aqueous systems, but are then desirably employed in  
substantially anhydrous systems. Much effort is made to dehydrate, i.e., remove  
water from, chemical components in such chemical systems, and thereafter to keep  
such systems dry.

To provide chemicals and chemical systems having appropriately low water  
20 content, tedious drying procedures are often used. Chemicals can be commercially  
sold as spray-dried or tray-dried, giving them a water content of less than about  
5000 parts per million (ppm). Having such a relatively high water content can  
cause these materials to require additional drying by the purchaser, often achieved  
by rotary vacuum drying or vacuum oven drying, followed by special handling in  
25 dry rooms.

Known methods of removing water from chemical compositions can be  
tedious, relatively slow, costly, and can involve the use of flammable or hazardous  
solvents. A need exists to identify new processes for drying hydrous materials such  
as chemicals and articles of manufacture.

30

### Summary of the Invention

The invention provides a method for removing water from a hydrous substrate by contacting the hydrous substrate with a hydrofluorocarbon (HFC). Water of the hydrous substrate can be transferred to the hydrofluorocarbon (to  
5 become contained, e.g., dissolved or dispersed in the hydrofluorocarbon), and thereafter optionally and preferably removed from the HFC in any convenient and effective manner, the net effect being a reduction in the concentration of water associated with the hydrous substrate. Water can be removed from the HFC mechanically, by volatilization (e.g., distillation, azeotropic distillation, boiling,  
10 etc.), or by any other useful method. Preferred hydrofluorocarbons include hydrofluoroethers (HFEs).

For purposes of the present description, a chemical composition, e.g., a mixture or solution, containing hydrous substrate and hydrofluorocarbon (i.e., containing substrate, water, and HFC), will be referred to as a "hydrous HFC  
15 composition." Water can be removed from the hydrous HFC composition, generally with HFC also being removed, to result in a dehydrated HFC composition containing substrate, hydrofluorocarbon, and a reduced amount of water, preferably no more than a residual amount of water, and most preferably substantially no water.

20 The method can be used to dehydrate a variety of different substrates, and is particularly useful for dehydrating chemical compositions including an aqueous solution of an electrolyte salt. Optionally, an organic solvent can also be present in the aqueous salt solution.

An HFC (such as an HFE) as a solvent medium in a dehydration process can  
25 exhibit low ozone depletion and reduced global warming effects. Moreover, the dehydration process can be more efficient than dehydration processes that use other solvents such as perfluorocarbons. Additionally, the use of HFCs to dehydrate chemical compositions has been found to provide a dehydration product with an appearance that is more aesthetically pleasing than such products dehydrated using  
30 other common organic solvents (PFCs or CFCs), or other dehydration techniques (spray drying or oven drying). Specifically, some chemical substrates dehydrated

using an HFE solvent have been found to exhibit relatively improved appearance, including an attractive pearlescent appearance (as a solid or in the form of a solution or slurry), and as a solid have the attractive appearance of a flaky, flowable solid with uniform consistency. In contrast, like substrates dehydrated by methods such as oven or spray drying can be of a less attractive, less flowable, less uniform consistency (e.g., coalesced, chunky, non-uniformly textured), of a relatively higher density, and not flaky but typically of a chunky or cube-like or agglomerated cube-like structure.

An aspect of the invention relates to a method of dehydrating a hydrous substrate. The method includes the steps of combining the hydrous substrate with a hydrofluorocarbon to form a hydrous hydrofluorocarbon composition, and volatilizing the hydrous hydrofluorocarbon composition.

A further aspect of the invention relates to a method of dehydrating a water-containing substrate. The method comprises the steps of providing a water-containing substrate comprising substrate and water, and adding hydrofluorocarbon to the water-containing substrate to provide a hydrous hydrofluorocarbon composition comprising substrate, water, and hydrofluorocarbon. Optionally, water can be removed from the hydrous hydrofluorocarbon composition, by any desired method, to provide a dehydrated hydrofluorocarbon composition comprising hydrofluorocarbon, substrate, and a reduced amount of water, preferably no more than a residual amount of water.

Yet a further aspect of the invention relates to a method of dehydrating a hydrous substrate comprising a fluorinated chemical salt and optionally an organic solvent. The method includes the steps of combining the hydrous substrate with hydrofluoroether to form a hydrous hydrofluoroether composition, azeotropically distilling the hydrous hydrofluoroether composition to volatilize water and the hydrofluoroether therein. This removes water from the hydrous hydrofluoroether composition and produces a dehydrated hydrofluoroether composition having a reduced water content. A polar organic solvent can optionally be added to the dehydrated hydrofluoroether composition, and the hydrofluoroether can optionally be separated from the polar organic solvent.

As used within the present description, the prefix “perfluoro-,” and the term “perfluorinated,” refer to organic carbon backbone-based molecules typically containing carbon-bonded hydrogen atoms, but wherein substantially all (e.g., at least 90%, preferably at least 95%) of the carbon-bonded hydrogen atoms have  
5 been replaced by fluorine atoms.

### **Brief Description of the Drawings**

Figure 1 illustrates an embodiment of the present invention wherein a hydrous substrate is contacted with an HFC to form a hydrous HFC composition,  
10 and HFC and water are removed from the hydrous HFC composition by azeotropic distillation.

### **Detailed Description**

According to the method of the invention, a hydrous substrate can be  
15 combined with a hydrofluorocarbon to form a hydrous hydrofluorocarbon composition (“hydrous HFC composition”). For purposes of the present description the term “hydrous substrate” means any solution, mixture, suspension, emulsion, or other material or combination of materials containing water and a substrate, with the water contacting, containing, or being contacted by or contained  
20 by, or on the surface of, the substrate. The term “water-containing substrate” means a particular type of hydrous substrate wherein water is contained within the substrate, as opposed to water contacting an exposed surface of the substrate in a manner that would allow removal or drying of the surface water by solvent displacement. A water-containing substrate can include solid or liquid materials in  
25 the form of a solution, suspension, mixture, emulsion, etc., and can contain water, e.g., in the form of dissolved, dispersed, or absorbed water, water of hydration, or any other form of water present other than on an exposed surface of the substrate.

The substrate can in general be any material at all, and can be organic or inorganic, natural or synthetic, and can be in the form of a solid, a liquid, or an  
30 article of manufacture. Preferably the substrate can be substantially non-reactive with the hydrofluorocarbon chosen for use with the dehydration method, and can be

substantially thermally stable (e.g., will not degrade to an unacceptable degree) at the volatilization temperature. The substrate can include a liquid chemical such as a polar organic solvent, an alcohol, or polyol; another type of liquid such as a liquid fluorochemical; a solid such as a solid article of manufacture or a solid chemical composition which can be, e.g., in a granular form or the form of a powder, a  
5 polymer or polymeric material, or a synthetic or natural material like a plant or a natural or synthetic fiber; or mixtures of these or other forms of materials. More specifically, the substrate can comprise a liquid, a solid, a dispersed or dissolved chemical composition (e.g., an alkali metal hydroxide such as lithium hydroxide  
10 monohydrate, an alkali metal halide, e.g., potassium fluoride or cesium fluoride, or an alkali metal imide), a wet or damp solid, (e.g., a powder such as a cosmetic or a magnetic powder), an aqueous slurry, an aqueous solution, a water-contaminated polar organic solvent, or a water-containing emulsion.

The process can be useful to remove water from a single hydrous substrate,  
15 or a mixture or combination of substrates. For example, the process can be useful for removing water from a chemical composition that contains water, but is otherwise relatively pure. Alternatively, the process can be useful for removing water from a mixture of a hydrous chemical composition contained, e.g., dissolved, suspended, or in admixture with, an organic solvent. The organic solvent may or  
20 may not be water-miscible or water-soluble, and may or may not be miscible or soluble in a chosen HFC.

In one preferred embodiment of the process, the substrate can comprises a hydrous, ionizable, hygroscopic, light metal salt that can be in the form of a solid, or that can be dissolved, suspended, or in admixture with an organic solvent.  
25 Examples of such light metal salts include alkali metal, alkaline earth metal, ammonium, and Group IIIB metal (e.g., aluminum) salts of anions such as  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{ClO}_4^-$ ,  $\text{SbF}_6^-$ ,  $\text{R}_f\text{SO}_3^-$ , where  $\text{R}_f$  is a perfluoroalkyl group preferably of one to about 12 carbon atoms, more preferably 1 to about 4 carbon atoms; the bis(perfluoroalkanesulfonyl)imide anion,  $(\text{R}_f\text{SO}_2)_2\text{N}^-$ , where  $\text{R}_f$  and  $\text{R}'_f$  are  
30 independently selected from perfluoroalkyl groups preferably of 1 to about 12 carbon atoms, more preferably 1 to about 8 carbon atoms;

bis(perfluoroalkylsulfonyl)methide anion,  $(R_fSO_2)C^-(R)(SO_2R'_f)$ , where  $R_f$  and  $R'_f$  are independently selected from perfluorinated alkyl groups preferably of 1 to about 12 carbon atoms, more preferably 1 to about 4 carbon atoms, and R is H, Br, Cl, I, alkyl of 1 to about 20 carbon atoms, alkenyl of 3 to 4 carbon atoms, aryl, or alkaryl;  
 5 and the tris(perfluoroalkanesulfonyl)methide anion,  $(R_fSO_2)C^-(SO_2R'_f)(SO_2R''_f)$ , where  $R_f$ ,  $R'_f$  and  $R''_f$  are independently selected from perfluorinated alkyl groups preferably of 1 to about 12 carbon atoms, more preferably one to about 4 carbon atoms. Such salts also include cyclic perfluoroaliphaticdisulfonimide salts such as those described in U.S. Pat. No. 4,387,222 (Kosher), and metal salts of acids such  
 10 as those described by DesMarteau et al. in J. Fluor. Chem. 45, 24 (1989).

Representative examples of light metal salt substrates include  $LiOH \cdot H_2O$ ,  $CF_3SO_3Li$ ,  $C_2F_5SO_3Li$ ,  $C_8F_{17}SO_3Li$ ,  $C_{10}F_{21}SO_3Li$ ,  $(CF_3SO_3)_2Ba$ ,  $(CF_3SO_2)_2NNa$ ,  $(C_2F_5SO_2)_2NLi$ ,  $(C_4F_9SO_2)(CF_3SO_2)NLi$ ,  $[(CF_3SO_2)_2N]_3Al$ ,  $(CF_3SO_2)_2C(H)Li$ ,  $(CF_3SO_2)_2NLi$ ,  $cyclo(CF_2SO_2)_2NLi$ ,  $cyclo-(CF_2SO_2)_2C(H)Li$ ,  $(CF_3SO_2)_3CLi$ ,  
 15  $(CF_3)_2NC_2F_4SO_3Li$ ,  $[(CF_3)_2NC_2F_4SO_2]_2NLi$ ,  $(C_8F_{17}SO_2)(CF_3SO_2)NLi$ ,  $CF_3SO_2(C_6H_5SO_2)NLi$ ,  $(CF_3SO_2)(NC)_2CLi$ , phosphorus salts, and mixtures thereof.

Representative solvent substrates, e.g., those that can be useful in battery electrolytes, include aprotic solvents which are dry, i.e., solvents which have a water content less than about 100 ppm, preferably less than about 50 ppm.  
 20 Examples of suitable aprotic electrolyte solvents include linear ethers such as diethyl ether, diethylene glycol dimethyl ether, and 1,2-dimethoxyethane; cyclic ethers such as tetrahydrofuran, 2-methyltetrahydrofuran, dioxane, dioxolane, and 4-methyldioxolane; esters such as methyl formate, ethyl formate, methyl acetate, dimethyl carbonate, diethyl carbonate, propylene carbonate, ethylene carbonate, and  
 25 butyrolactones (e.g. gamma butyrolactone); nitriles such as acetonitrile and benzonitrile; nitro compounds such as nitromethane or nitrobenzene; amides such as N,N-dimethylformamide, N,N-diethylformamide, and N-methylpyrrolidinone; sulfoxides such as dimethyl sulfoxide; sulfones such as dimethylsulfone; tetramethylene sulfone, and other sulfolanes; oxazolidinones such as N-methyl-2-  
 30 oxazolidinone; and mixtures thereof.



Preferably, the electrolyte solvent is selected from the group consisting of propylene carbonate, ethylene carbonate, dimethyl carbonate, diethylene glycol dimethyl ether and 1,2-dimethoxyethane.

5 The hydrous substrate can contain any amount of water, generally from about 50 parts per million (ppm) up to about 99 percent by weight water, often from about 100 ppm to about 50 weight percent water. The water can be in the form of free water, dispersed water, surface water, water as a solvent or solute, or water of hydration. Preferably, for the sake of efficiency, the method can include the step of removing as much water as is feasible from the substrate, e.g., by  
10 mechanical methods, prior to combining the hydrous substrate with hydrofluorocarbon to form a hydrous HFC composition. Suitable mechanical methods can include centrifugal methods, filtering methods, etc., or chemical methods such as desiccants, phase separations, extractions, etc.

The term "hydrofluorocarbon" means an organic chemical compound  
15 minimally containing a carbon backbone substituted with carbon-bonded hydrogen and carbon-bonded fluorine atoms, and optionally containing one or more skeletal heteroatoms such as divalent oxygen, trivalent nitrogen, or hexavalent sulfur. The carbon backbone can be straight, branched, cyclic, or mixtures of these, but preferably includes no functional or unsaturated groups. This definition includes  
20 compounds having more than approximately 5 molar percent fluorine substitution, or less than 95 molar percent fluorine substitution, based on the total number of hydrogen and fluorine atoms bonded to carbon, and specifically excludes organic compounds generally referred to as perhalogenated compounds, perfluorinated compounds, and hydrocarbon (non-fluorinated) compounds.

25 Preferred hydrofluorocarbons can be capable of volatilization along with water, at a desired temperature and pressure, yet have neither so high a boiling point as to require large heat input to effect volatilization, nor so low a boiling point that unacceptable losses of the HFC occur due to its volatilization. Most preferably, the HFC, when it contains water (e.g., dispersed or dissolved water), has  
30 a vapor pressure that will provide a vapor evolving from the hydrous HFC composition (i.e., a hydrous HFC vapor), wherein the vapor has a concentration of

water, whether considered on a molar or weight basis, that is relatively higher than the concentration of water in the hydrous HFC composition. The particular hydrofluorocarbon chosen for use with a specific hydrous substrate in a particular dehydration process can be based on these properties of the hydrofluorocarbon at a particular range of temperature and pressure. Preferred hydrofluorocarbons can have a boiling point in the range from about 30°C to about 275°C, preferably from about 50°C to about 200°C, most preferably from about 50°C to about 110°C.

It can be especially desirable that the hydrofluorocarbon be non-flammable. This can mean that the HFC can have a flashpoint above 100 degrees Fahrenheit. To be non-flammable, the relationship between the number of fluorine, hydrogen, and carbon atoms can preferably be related in that the number of fluorine atoms per the number of combined hydrogen atoms and carbon-carbon bonds be less than or equal to about 0.8:

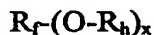
$$\# \text{ of F atoms} / (\# \text{ H atoms} + \# \text{ C-C bonds}) \geq 0.8$$

In general, increasing the number of fluorine atoms, decreasing the number of hydrogen atoms, or decreasing the number of carbon-carbon bonds, each increase the flashpoint of the HFC.

Preferred hydrofluorocarbons include hydrofluoroether compounds (also sometimes referred to as simply hydrofluoroethers, highly fluorinated ethers, or HFEs) which are chemical compounds minimally containing carbon, fluorine, hydrogen, one or more ether oxygen atoms, and optionally one or more additional heteroatoms within the carbon backbone, such as sulfur or nitrogen. The hydrofluoroether can be straight-chained, branched-chained, or cyclic, or a combination thereof, such as alkylcycloaliphatic, and is preferably free of unsaturation. The hydrofluoroether can preferably have from about 2 to about 20 carbon atoms. Preferred HFEs can be relatively low in toxicity, can have low ozone depletion potentials, e.g., zero, short atmospheric lifetimes, and a low global warming potential, e.g., relative to chlorofluorocarbons and many chlorofluorocarbon substitutes.

Preferred hydrofluoroethers include two identifiable varieties: segregated hydrofluoroethers, wherein ether-bonded alkyl or alkylene, etc., segments of the HFE are either perfluorinated (e.g., perfluorocarbon) or non-fluorinated (e.g., hydrocarbon), but not partially fluorinated; and omega-hydrofluoroalkylethers, wherein ether-bonded segments can be non-fluorinated (e.g., hydrocarbon), perfluorinated (e.g., perfluorocarbon), or partially fluorinated (e.g., fluorocarbon or hydrofluorocarbon).

Segregated hydrofluoroethers include hydrofluoroethers which comprise at least one mono-, di-, or trialkoxy-substituted perfluoroalkane, perfluorocycloalkane, perfluorocycloalkyl-containing perfluoroalkane, or perfluorocycloalkylene-containing perfluoroalkane compound. These HFEs are described, for example, in WO 96/22356, and can be represented below in Formula I:



(Formula I),

wherein:

x is from 1 to about 3, and  $R_f$  is a perfluorinated hydrocarbon group having a valency x, which can be straight, branched, or cyclic, etc., and preferably contains from about 2 to 15 carbon atoms, more preferably from about 3 to 12 carbon atoms, and even more preferably from about 3 to 10 carbon atoms;

in all cases,  $R_f$  can optionally comprise a terminal  $F_3S-$  group;

each  $R_h$  is independently a linear or branched alkyl group having from 1 to about 8 carbon atoms, a cycloalkyl-containing alkyl group having from 4 to about 8 carbon atoms, or a cycloalkyl group having from 3 to about 8 carbon atoms;

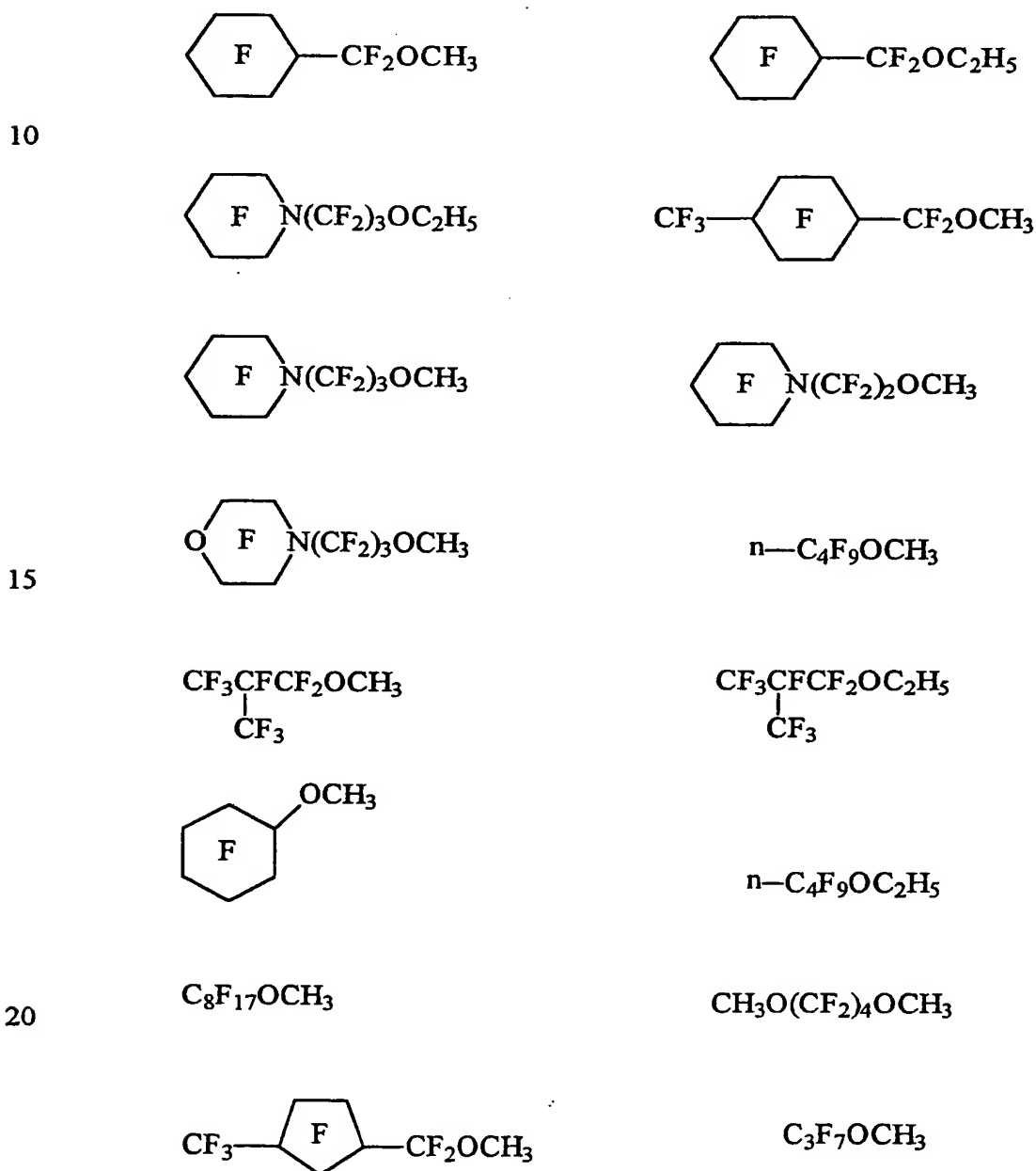
wherein either or both of the groups  $R_f$  and  $R_h$  can optionally contain one or more catenary heteroatoms;

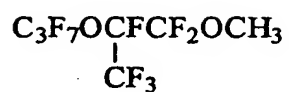
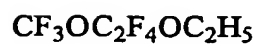
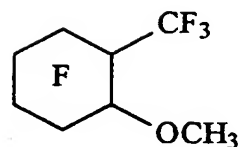
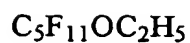
wherein the sum of the number of carbon atoms in the  $R_f$  group and the number of carbon atoms in the  $R_h$  group(s) is preferably greater than or equal to 4.

Preferably, x is 1;  $R_f$  is a perfluoroalkyl comprising from about 3 to 10 carbons, optionally containing one or more heteroatoms; and  $R_h$  is an alkyl group having from 1 to about 6 carbon atoms. Most preferably, x is 1;  $R_f$  is a linear or

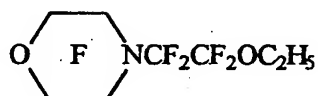
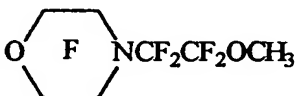
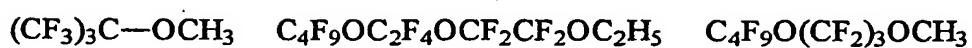
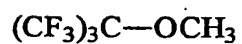
- branched perfluoroalkyl groups having from 3 to about 8 carbon atoms; a perfluorocycloalkyl-containing perfluoroalkyl group having from 5 to about 8 carbon atoms; or a perfluorocycloalkyl group having from about 5 to 6 carbon atoms;  $R_h$  is an alkyl group having from 1 to about 3 carbon atoms; and  $R_f$  but not  $R_h$  can contain one or more heteroatoms.

Representative hydrofluoroether compounds described by Formula I include the following:

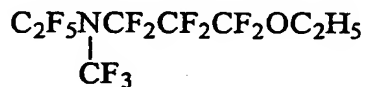
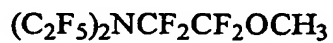
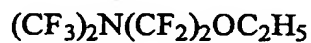
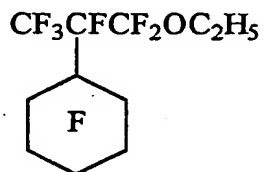
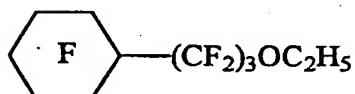


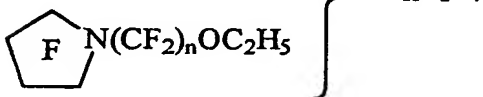
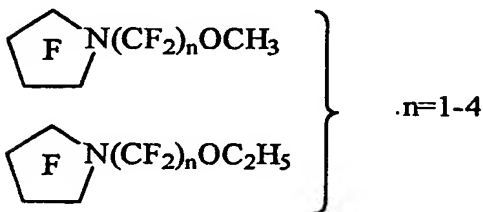
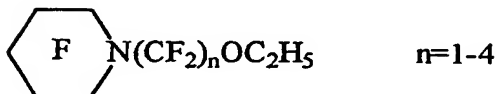
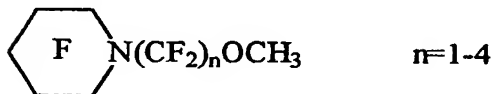
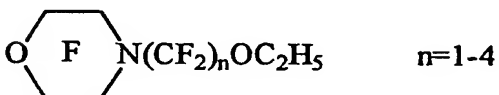
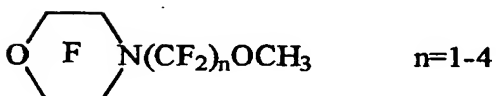
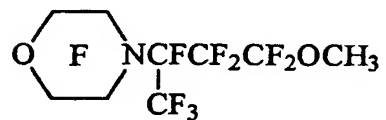
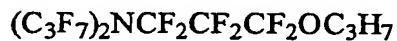
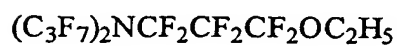
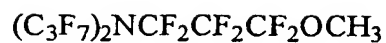


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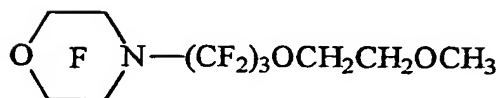
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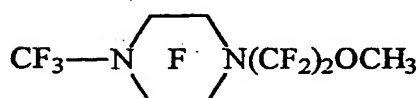
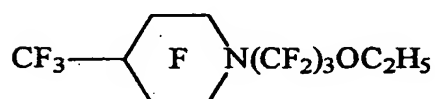
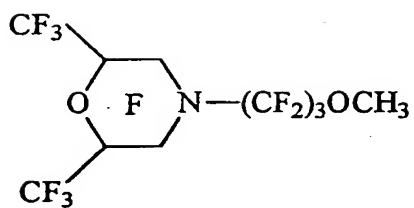




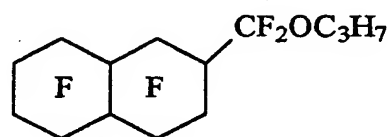
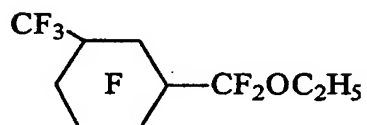
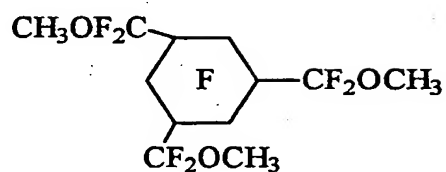
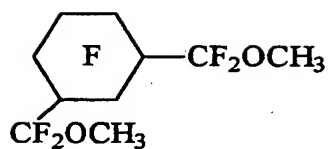
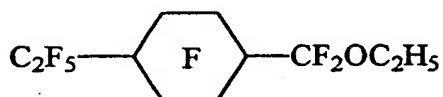
$$n=1-4$$

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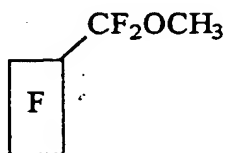
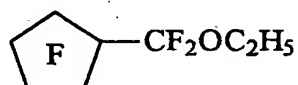
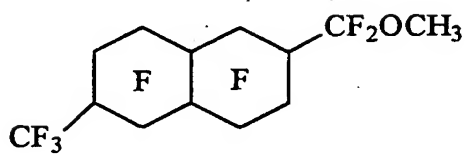


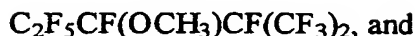


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wherein cyclic structures designated with an interior "F" are perfluorinated. These HFE compounds can be used alone or in admixture with another HFE.

- 5        Particularly preferred segregated hydrofluoroethers of Formula I include n-C<sub>3</sub>F<sub>7</sub>OCH<sub>3</sub>, (CF<sub>3</sub>)<sub>2</sub>CFOCH<sub>3</sub>, n-C<sub>4</sub>F<sub>9</sub>OCH<sub>3</sub>, (CF<sub>3</sub>)<sub>2</sub>CFCF<sub>2</sub>OCH<sub>3</sub>, n-C<sub>4</sub>F<sub>9</sub>OC<sub>2</sub>H<sub>5</sub>, (CF<sub>3</sub>)<sub>2</sub>CFCF<sub>2</sub>OC<sub>2</sub>H<sub>5</sub>, (CF<sub>3</sub>)<sub>3</sub>COCH<sub>3</sub>, CH<sub>3</sub>O(CF<sub>2</sub>)<sub>4</sub>OCH<sub>3</sub>, CH<sub>3</sub>O(CF<sub>2</sub>)<sub>6</sub>OCH<sub>3</sub>, and mixtures thereof.

- Segregated hydrofluoroethers can be prepared by alkylation of
- 10        perfluorinated alkoxides prepared by the reaction of a corresponding perfluorinated acyl fluoride or perfluorinated ketone with an anhydrous alkali metal fluoride (e.g., potassium fluoride or cesium fluoride) or anhydrous silver fluoride in an anhydrous polar aprotic solvent. (See, e.g., the preparative methods described in French Patent Publication No. 2,287,432 and German Patent Publication No. 1,294,949).
- 15        Alternatively, a fluorinated tertiary alcohol can be allowed to react with a base (e.g., potassium hydroxide or sodium hydroxide) to produce a perfluorinated tertiary alkoxide which can then be alkylated by reaction with alkylating agent, such as described in U.S. Pat. No. 5,750,797, which is herein incorporated by reference.

- Suitable alkylating agents for use in the preparation of segregated
- 20        hydrofluoroethers include dialkyl sulfates (e.g., dimethyl sulfate), alkyl halides (e.g., methyl iodide), alkyl p-toluenesulfonates (e.g., methyl p-toluenesulfonate), alkyl perfluoroalkanesulfonates (e.g., methyl perfluoromethanesulfonate), and the like. Suitable polar aprotic solvents include acyclic ethers such as diethyl ether, ethylene glycol dimethyl ether, and diethylene glycol dimethyl ether; carboxylic acid esters
- 25        such as methyl formate, ethyl formate, methyl acetate, diethyl carbonate, propylene carbonate, and ethylene carbonate; alkyl nitrites such as acetonitrile; alkyl amides such as N,N-dimethylformamide, N,N-diethylformamide, and N-methylpyrrolidone;



alkyl sulfoxides such as dimethyl sulfoxide; alkyl sulfones such as dimethylsulfone, tetramethylene sulfone, and other sulfolanes; oxazolidones such as N-methyl-2-oxazolidone; and mixtures thereof.

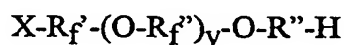
Suitable perfluorinated acyl fluorides can be prepared by electrochemical fluorination (ECF) of the corresponding hydrocarbon carboxylic acid (or a derivative thereof), using either anhydrous hydrogen fluoride (Simons ECF) or KF<sub>2</sub>HF (Phillips ECF) as the electrolyte. Perfluorinated acyl fluorides and perfluorinated ketones can also be prepared by dissociation of perfluorinated carboxylic acid esters (which can be prepared from the corresponding hydrocarbon or partially-fluorinated carboxylic acid esters by direct fluorination with fluorine gas). Dissociation can be achieved by contacting the perfluorinated ester with a source of fluoride ion under reacting conditions (see the method described in U.S. Pat. No. 3,900,372 (Childs), the description of which is incorporated herein by reference) or by combining the ester with at least one initiating reagent selected from the group consisting of gaseous, nonhydroxylic nucleophiles; liquid, nonhydroxylic nucleophiles; and mixtures of at least one non-hydroxylic nucleophile (gaseous, liquid, or solid) and at least one solvent which is inert to acylating agents.

Initiating reagents which can be employed in the dissociation are those gaseous or liquid, non-hydroxylic nucleophiles and mixtures of gaseous, liquid, or solid, nonhydroxylic nucleophile(s) and solvent (hereinafter termed "solvent mixtures") which are capable of nucleophilic reaction with perfluorinated esters. The presence of small amounts of hydroxylic nucleophiles can be tolerated. Suitable gaseous or liquid, nonhydroxylic nucleophiles include dialkylamines, trialkylamines, carboxamides, alkyl sulfoxides, amine oxides, oxazolidones, pyridines, and the like, and mixtures thereof. Suitable non-hydroxylic nucleophiles for use in solvent mixtures include such gaseous or liquid, non-hydroxylic nucleophiles, as well as solid, non-hydroxylic nucleophiles, e.g., fluoride, cyanide, cyanate, iodide, chloride, bromide, acetate, mercaptide, alkoxide, thiocyanate, azide, trimethylsilyl difluoride, bisulfite, and bifluoride anions, which can be used in the form of alkali metal, ammonium, alkyl-substituted ammonium (mono-, di-, tri-, or tetra-substituted), or quaternary phosphonium salts, and mixtures thereof. Such

salts are in general commercially available but, if desired, can be prepared by known methods, e.g., those described by M. C. Sneed and R. C. Brasted in Comprehensive Inorganic Chemistry, Volume Six (The Alkali Metals), pages 61-64, D. Van Nostrand Company, Inc., New York (1957), and by H. Kobler et al. in Justus Liebigs Ann. Chem. 1978, 1937. 1,4-diazabicyclo[2.2.2]octane and the like are also suitable solid nucleophiles.

Other useful hydrofluoroethers include omega-hydrofluoroalkyl ethers such as those described in U.S. Patent No. 5,658,962 (Moore et al.), incorporated herein by reference, which can be described by the general structure shown in Formula II:

10



(Formula II)

wherein:

X is either F or H;

15  $R_f'$  is a divalent perfluorinated organic radical having from 1 to about 12 carbon atoms;

$R_f''$  is a divalent perfluorinated organic radical having from 1 to about 6 carbon atoms;

$R''$  is a divalent organic radical having from 1 to 6 carbon atoms, and is preferably perfluorinated; and

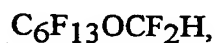
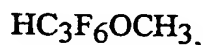
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y is an integer from 0 to 4;

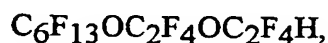
wherein when X is F and y is 0,  $R''$  contains at least one F atom.

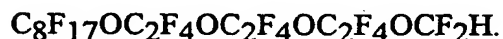
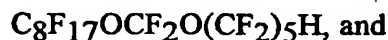
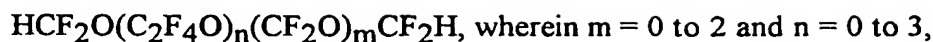
Representative compounds described by Formula II which are suitable for use in the processes of the invention include the following compounds:

25

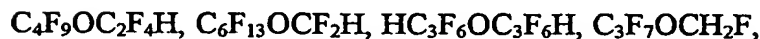


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10 Preferred omega-hydrofluoroalkyl ethers include  $\text{C}_4\text{F}_9\text{OC}_2\text{F}_4\text{H}$ ,



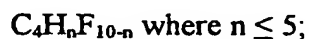
$\text{HCF}_2\text{O}(\text{C}_2\text{F}_4\text{O})_n(\text{CF}_2\text{O})_m\text{CF}_2\text{H}$  wherein  $m$  is from 0 to 2 and  $n$  is from 0 to 3, and mixtures thereof.

Omega-hydrofluoroalkyl ethers described by Formula II can be prepared by  
 15 decarboxylation of the corresponding precursor fluoroalkyl ether carboxylic acids and salts thereof or, preferably, the saponifiable alkyl esters thereof, as described in U.S. Pat. No. 5,658,962, which is incorporated herein by reference. Alternatively, omega-hydrofluoroalkyl ethers can be prepared by reduction of a corresponding  
 20 omega-chlorofluoroalkyl ether (e.g., those omega-chlorofluoroalkyl ethers described in WO 93/11868 published application), which is also described in U.S. Pat. No. 5,658,962.

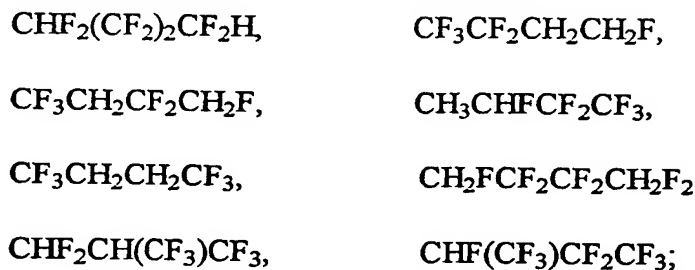
Other hydrofluorocarbons can include non-ether HFCs selected from the following groups:

(1) linear or branched compounds of the formula:

25

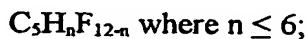


representative examples of this class are:

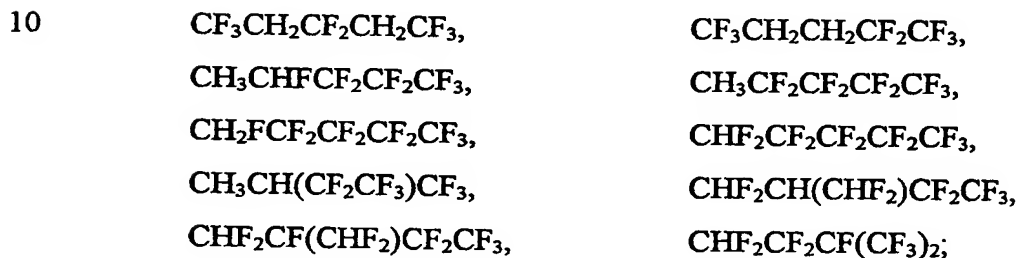


(2) linear or branched compounds of the empirical formula:

5

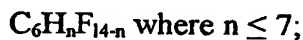


representative examples of this class are:



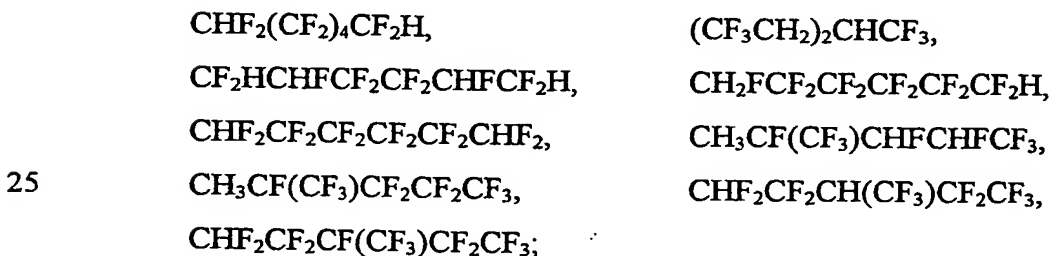
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(3) linear or branched compounds of the empirical formula:



20

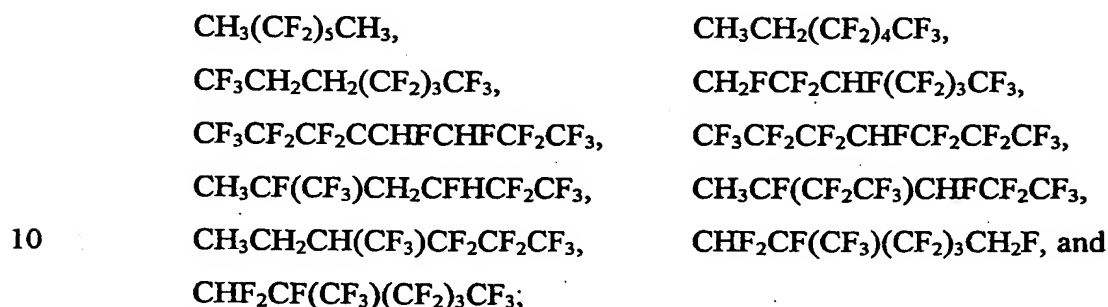
representative examples of this class are:



- (4) linear or branched compounds of the empirical formula:



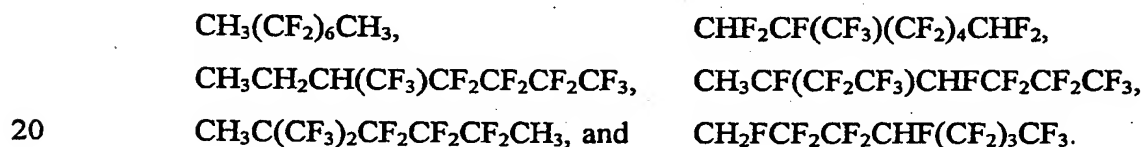
- 5 representative examples of this class are:



- (5) linear or branched compounds of the empirical formula



- representative examples of this class are:



The hydrofluorocarbon can be used alone, as a mixture of two or more hydrofluorocarbons, or in admixture with one or more other ingredients such as another volatile co-solvent. A surfactant (other than a surfactant which may be present as substrate) can be included in the hydrofluorocarbon, but is not necessary for many applications of the method, and may preferably be absent for many applications, especially where high purity of the dehydrated substrate is desired.

According to the method of the invention a hydrofluorocarbon can be combined, mixed, or otherwise contacted with a hydrous substrate to provide a hydrous HFC composition; e.g., a hydrofluoroether can be contacted with a hydrous substrate to provide a hydrous hydrofluoroether composition (hydrous

HFE composition). Upon combining the hydrous substrate with the HFC, water is removed from the hydrous substrate and transfers to and is thereafter contained (e.g., dispersed, dissolved, or otherwise present) in the HFC.

5 The hydrous substrate and the hydrofluorocarbon can combine to form various forms of hydrous HFC compositions. If the substrate is completely miscible in the HFC, the hydrous HFC composition can be a single phase of the HFC and dissolved substrate. If the substrate comprises either an immiscible solvent or an insoluble solid, the hydrous HFC composition can contain the HFC phase and one phase for each of the immiscible solvent and insoluble solid, establishing two or  
10 three phases. Additionally, given a sufficient amount of water in the hydrous substrate, there can be a separate aqueous phase which may exist initially and subside as the dehydration process progresses. A typical hydrous HFC composition can comprise at least two phases: 1) an aqueous phase containing water, substrate, and if present and if water soluble, organic solvent; and 2) an HFC phase containing  
15 hydrofluorocarbon and water. If the substrate includes a water-insoluble organic solvent, the hydrous HFC composition may comprise a ternary system with organic solvent being an additional phase. The phases may be present in the form of an emulsion, although this may be unpreferred because in practice an emulsion may be difficult to handle or process. Also, the hydrous HFC composition may be  
20 susceptible to foaming, but foaming will preferably be minimized.

The amounts of each phase in the hydrous HFC composition can be controlled and optimized to provide an efficient process. Typically, water will be contained, e.g., dissolved or dispersed, in each of the phases.

25 The water will typically be contained in the HFC as a dissolved solute or as a dispersed phase. Generally, whether or not a dispersed phase of water is present, water will be in equilibrium with the HFC and dissolved in the HFC up to a saturation level. The amount of water dissolved or dispersed in the HFC will depend on various factors such as the solubility of water in the HFC at the processing temperature. Water can be dissolved in HFCs, at equilibrium, at various  
30 levels, depending on temperature and the HFC (its affinity to dissolve water). Typical saturation concentrations of water in an HFE, for example, can be less than

about 100 parts per million (ppm) water by weight, e.g., less than 60 ppm or 15 ppm. The HFC may contain dissolved or dispersed water when introduced to the hydrous substrate, or, as can be preferred, the HFC can be substantially free of water when introduced to the hydrous substrate. In either case, water will transfer  
5 from the hydrous substrate to the HFC, and can be removed from the aqueous HFC composition system as desired.

The amount of hydrofluorocarbon relative to the hydrous substrate in the hydrous HFC composition can be chosen based on factors such as the solubility of water in the hydrofluorocarbon, the amount of water understood to be associated  
10 with the hydrous substrate, desired or actual process conditions (e.g., process parameters such as temperature, pressure, and whether the process is a batch or a continuous process), the amount of water desired to be removed from the hydrous substrate, and the amount of water acceptably contacting, associated with, or present in the substrate after performing the dehydration process. The hydrous  
15 HFC composition should contain enough hydrofluorocarbon to remove, through a batch or continuous process, a significant portion of, and preferably, substantially all of the water initially associated with the hydrous substrate. Although the following ranges are not intended to be limiting, and these ranges can change or be adjusted according to factors such as those listed above, the hydrous HFC composition can  
20 preferably contain from about 30 to about 90 parts by weight hydrofluorocarbon per 100 parts by weight of the hydrous HFC composition, (i.e., the combined parts by weight of hydrous substrate (substrate and water) and hydrofluorocarbon), more preferably from about 50 to about 80 parts by weight hydrofluorocarbon based on 100 parts hydrous HFC composition.

25 With removal of HFC during the removal step, as detailed below, additional HFC can be introduced to the hydrous HFC composition, with the additional HFC containing water, or, preferably, being free or substantially free of water.

The hydrous HFC composition can be prepared by combining the hydrous substrate and hydrofluorocarbon in any manner, such as in a kettle or other vessel  
30 adapted to facilitate the dehydration process. (The kettle or other vessel will be referred to herein for convenience as the "vessel.") The process can be practiced in

a continuous, a batch, or a semi-batch method, in vessels properly adapted for any of these. Preferably the hydrous substrate and the hydrofluorocarbon can be intimately contacted to facilitate removal of water from the hydrous substrate by dissolution or dispersion of the water in the hydrofluorocarbon. The vessel can  
5 preferably be equipped with a stirrer to enable agitation of the contents and uniform mixing. Preferred vessels can also preferably be equipped with an inert gas inlet and outlet to enable blanketing of the contents of the vessel with a dry, inert gas, and can additionally be equipped to allow a continuous dehydration process by being fitted with a condenser arranged so that condensate can be directed to a receiver or  
10 preferably a decanter. The vessel can also preferably be fitted with a heating or a cooling jacket, internal heating or cooling coils, or other means to transfer heat energy into or out of the hydrous HFC composition.

Once prepared, water can be removed from the hydrous HFC composition by any convenient, effective, or otherwise desired or suitable method. Because the  
15 hydrous HFC composition contains water (e.g., a water phase of the hydrous HFC composition, or water dispersed in the HFC) in contact with an HFC phase, some generally small amount of water will typically dissolve in the HFC phase to a level of saturation. This being true, the process allows for removal of water from the hydrous substrate by transfer of water from the hydrous substrate to the HFC, and  
20 optionally and preferably the additional step of removing water from the HFC, or removing water-containing HFC (i.e., the HFC phase) from the hydrous HFC composition. In a continuous or semi-continuous process, the water-containing HFC phase can be removed, and can optionally and preferably be replaced with relatively drier HFC to maintain a concentration gradient between the hydrous  
25 substrate and the HFC phase, resulting in mass transfer of water from the hydrous substrate to the HFC phase for removal.

By "removed" it is meant that water, and generally HFC, can be taken away or otherwise allowed, forced, or encouraged to depart from the hydrous HFC composition, for example by mechanical or chemical separation methods,  
30 volatilization, refluxing, azeotroping, evaporation, distillation (e.g., azeotropic distillation), etc. of the HFC and water (e.g., the HFC phase of the hydrous HFC



composition). Because water is contained in the HFC phase, any type of mechanical or chemical method of removing the HFC phase will accomplish the water-removal step. As is evident, the water-removal step will typically be accomplished by removal of a portion of HFC, meaning simultaneous removal of  
5 both HFC and water from the hydrous HFC composition.

As a preferred method of removing water from a hydrous HFC composition, water, in the form of water dissolved in the HFC phase, can be removed as a vapor (e.g., volatilized, evaporated, azeotroped, distilled, etc.), under desired conditions of reduced or elevated temperature and reduced or elevated pressure. The pressure  
10 within the vessel can be reduced, and/or the temperature can be increased to effect volatilization of HFC and water in the HFC phase. Alternatively, the temperature of the hydrous HFC composition can be reduced by cooling, and the pressure reduced to effect volatilization. Reduced temperature can be desired in situations where a component of the hydrous HFC composition (e.g., the substrate or the  
15 HFC) is temperature sensitive. Often, the hydrous HFC composition can be heated to a temperature sufficient to initiate volatilization of water and hydrofluorocarbon by distillation at atmospheric pressure, under vacuum, or under greater than atmospheric pressure. The actual temperature and pressure employed in any particular dehydration process may vary, and may be chosen based on factors such  
20 as the particular hydrous substrate to be dried and the chosen hydrofluorocarbon. While either elevated or reduced pressures or temperatures may be useful, preferred volatilization temperatures can be in the range from about 50 to 150°C, or from about 50 to 110°C. It is possible for the hydrous HFC composition to reach a boil, although this is not generally preferred, and volatilization can be effected without  
25 boiling.

During volatilization, HFC and water from the hydrous HFC composition evolve to form a hydrous HFC vapor phase comprising gaseous HFC and water vapor. The relative amounts of water and HFC vapor contained in the vapor phase will depend on the amounts of each component in the hydrous HFC composition,  
30 and the relative volatility of each component. In general, because of the azeotropic nature of a composition containing water and HFC, it has been found to be possible

and preferable for the hydrous HFC vapor phase to have a higher concentration of water vapor than the concentration of water in the liquid HFC phase (when considered either on a weight or molar basis). This can be preferable because it enables, e.g., in a continuous process, condensation of the vapor phase to a two-  
5 phase liquid system. (If the concentration of water in the vapor phase were less than in the liquid phase, where water is dissolved in the HFC, the condensate would also be a single phase of water dissolved in HFC.) Separation of the organic HFC and aqueous phases of the condensate allows the HFC phase to be returned as a recycle stream to the hydrous HFC composition.

10 In such a continuous system, because the aqueous and the HFC phases of the condensate will be in equilibrium, the recycle HFC stream will typically contain dissolved water, possibly to a level of saturation. An optional and preferred, but not required, step of the process can be included, if desired, e.g., to accelerate removal of water from the substrate. This step includes further treating the HFC  
15 recycle stream to remove some or all of the water in the recycled HFC phase. When the treated recycled HFC is returned to the hydrous HFC composition, the concentration of water in the HFC phase of the hydrous HFC composition is further reduced, thereby allowing more water from the hydrous substrate to transfer into the HFC of the hydrous HFC composition, and further reducing the concentration  
20 of water associated with the hydrous substrate. This optional HFC drying step can be accomplished by known methods of drying liquid chemicals, for example by contacting the recycled HFC phase with a conventional solid drying agent such as a molecular sieve, anhydrous magnesium sulfate, anhydrous calcium chloride or Drierite™ drying agent (available from W. A. Hammond Drierite Co., Xenia, Ohio),  
25 or the like.

In a preferred embodiment of the method, water can be removed from a hydrous HFC composition by continuous azeotropic distillation, with the hydrous HFC vapor phase being condensed and allowed to separate into a two-phase condensate, and with the HFC portion of the condensate being separated and  
30 redirected back to the hydrous HFC composition as recycle. An example of such a preferred method is illustrated in Figure 1. In the Figure, vessel 2 includes hydrous

HFC composition 4, comprising HFC, substrate, and water. Hydrous HFC composition 4 is typically a multi-phase composition comprising an aqueous phase and an HFC phase. Hydrous HFC composition 4 is volatilized at desired conditions of temperature and pressure to produce hydrous HFC vapor 8, comprising HFC and water. Hydrous HFC vapor 8 can be condensed in condenser 10 to form condensate 12 having HFC phase 14 and aqueous phase 16. Preferably, the concentration of water in vapor phase 8 and condensate 12 is higher than the concentration of water in hydrous HFC composition 4. HFC phase 14 can be separated from condensate 12, optionally processed further to partially or fully remove any dissolved or dispersed water (the optional processing step is not shown in Figure 1), and then returned to hydrous HFC composition 4.

The water removal step can proceed until the water content of the hydrous substrate is desirably low for a particular substrate being dehydrated. Water content of the substrate can be measured directly by removing a sample of the substrate and using standard analytical methods such as spectroscopy, Karl Fischer titration, or a melting point measurement. Alternatively, water content of the substrate can be measured indirectly by monitoring the water content of the HFC phase.

When the water content of the hydrofluorocarbon has been reduced to an acceptable level, any water phase of the hydrous HFC composition has substantially subsided and departed, leaving a dehydrated HFC composition. The dehydrated HFC composition will comprise an HFC phase, substrate which may be dissolved in, dispersed in, or in admixture with the HFC phase, and may constitute or comprise a separate phase (the "substrate phase"), and will further typically contain a residual amount of water dissolved in one or more of the HFC phase, the substrate, and the substrate phase (if present). The residual water can be a relatively minor amount up to the saturation point of the HFC, and preferably is below an amount of water that would result in the presence of an aqueous phase. The amount of water present in the dehydrated HFC composition can depend on factors such as the duration and effectiveness of the water removal step, the identity of the substrate and its affinity to associate with water, the particular

hydrofluorocarbon used in the dehydration process and its ability to dissolve water at the given temperature and pressure, and the desired end application of the substrate and its tolerance for the presence of water, etc. For many applications the amount of water remaining in a dehydrated HFC composition will desirably be  
5 minimized and the dehydrated HFC composition will be essentially free of water, meaning that the dehydrated HFC composition contains substrate, HFC, and only a residual amount of water, e.g., less than 100 ppm.

After substantially complete removal of water from the hydrous HFC composition, what remains will be referred to as the dehydrated HFC composition.  
10 The dehydrated HFC composition will contain HFC, substrate, and substantially no water (as stated, each component or phase of the dehydrated HFC composition may contain a residual amount of water absorbed or dissolved therein). The dehydrated HFC composition will take the same form and have similar phases as the hydrated HFC composition, except that if an aqueous phase was present in the hydrated HFC  
15 composition, an aqueous phase will preferably not be present in the dehydrated HFC composition. If the substrate comprises an insoluble solid, a soluble solid, or a solvent that is miscible with the HFC, the dehydrated HFC composition will typically similarly contain the solid substrate, the dissolved solid, or the miscible solvent, respectively. If the substrate comprises a chemical (e.g., a salt) dissolved in  
20 an organic solvent immiscible with the HFC, the dehydrated HFC composition will typically contain two phases including an HFC phase and a separate solvent/dissolved salt phase.

The dehydrated HFC composition can preferably be brought to ambient temperature under a dry, inert gas atmosphere, for example, nitrogen or air, and the  
25 HFC can be separated from the dehydrated HFC composition to leave behind a dehydrated substrate. The dehydrated substrate will comprise the substrate, possibly a residual amount of water, and any other component not removed in the volatilization step, such as additives or impurities that were initially present in the hydrous substrate. The dehydrated substrate will typically take the form of the  
30 original substrate, e.g., a solid such as a powder, a liquid such as an organic solvent, or a combination of these.

The separation step, i.e., separation of the HFC from the dehydrated substrate, can be accomplished by separation methods that are well known and understood in the chemical art, including the use of liquid separation equipment and techniques, and mechanical separation equipment and techniques such as filtration, centrifuging, etc. The particular method chosen to accomplish the separation step can depend on factors such as the form of the substrate within the dehydrated HFC composition, e.g., whether the substrate is a solid or solvent, and whether the substrate is dissolved or dispersed in the composition.

Solid substrates can be separated from the HFC by mechanical methods such as filtration to leave a dry solid substrate. Again, dry means that the dehydrated substrate may contain a residual amount of absorbed or adsorbed water.

According to one embodiment of the method, a solid substrate (e.g., an electrolyte salt) dispersed in the dehydrated HFC composition may be separated from the HFC phase by adding an organic solvent to the dehydrated HFC composition to form a solvent solution of the salt dissolved or dispersed in a phase of the organic solvent, which can then be separated from the dehydrated HFC, e.g., by draining off the HFC phase. This embodiment of the process allows a solid dehydrated substrate to be directly transferred from the dehydrated hydrofluoroether composition to an organic solvent or other chemical treatment phase without transforming the substrate to the state of a dried solid. This embodiment can preferably be used for preparing a water sensitive or hygroscopic substrate, e.g., an electrolyte salt solution, because both the dehydration and the preparation of the salt solution are carried out within the environment of a dry liquid, perhaps under an inerting atmosphere, preventing contamination of the solid with water or undesirable gases.

The amount of water present in the dehydrated substrate is preferably minimized, and should be no more than a residual amount of water, i.e., an amount of water attracted to the substrate when in equilibrium with the HFC, with the HFC containing no more than a residual amount of water. The actual amount of water remaining any dehydrated substrate will depend on the amount of water remaining in the dehydrated HFC composition, and the affinity for the substrate to attract

water dissolved in the dehydrated HFC composition. As exemplary amounts of water preferably remaining in a dehydrated substrate, for applications of dehydrating electrolytes useful in electrical storage cells, the water content of the dehydrated electrolyte (optionally in solvent) can generally be less than about 100 ppm, preferably less than about 50 ppm.

In a preferred embodiment of the invention, the hydrated substrate and the dehydrated substrate both comprise an organic solvent with a salt dispersed or dissolved therein. An advantage to this method is that, as opposed to other drying processes (e.g., tray drying with heat), water can be removed from the salt without any process step wherein the salt has to be transformed into the state of a solid, but can be dissolved or dispersed in a solvent, preferably a dry solvent, throughout the dehydration process, with the dried substrate being dissolved in a dry solvent. A further advantage of this embodiment is that it provides an aesthetically pleasing dehydrated substrate, and does not cause caking or hardening of the substrate, thus eliminating the need for grinding or pulverization the otherwise dried, dehydrated solid.

This invention is further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to limit this invention. All parts are by weight unless otherwise stated. All determinations of water content in the examples were performed by Karl Fischer titration using a 652 KF Coulometer instrument made by Metrohm of Switzerland and distributed by Brinkmann Instruments in the U.S.A.

25

### EXAMPLES

**Preparation of Perfluorobutyl Methyl Ether ( $C_4F_9OCH_3$ )** – a 20 gallon (3.8 L) Hastalloy C reactor, equipped with stirrer and a cooling system, was charged with 6.0 kg (103.1 mol) of spray-dried potassium fluoride. The reactor was sealed, and the pressure inside the reactor was reduced to less than 100 torr. 25.1 kg of anhydrous dimethyl formamide was then added to the reactor, and the reactor was cooled to below 0°C with constant agitation. 25.1 kg (67.3 mol) of

heptafluorobutyryl fluoride (58% purity) was added to the reactor. When the temperature of the contents of the reactor reached -20°C, 12 kg (95.1 mol) of dimethyl sulfate was added to the reactor over a period of approximately 2 hours. The resulting mixture was then allowed to react for 16 hours with continuous agitation, the temperature was raised to 50°C for an additional 4 hours to facilitate complete reaction, and the temperature was cooled to 20°C. After cooling, volatile material (primarily perfluorooxacyclopentane present in the starting heptafluorobutyryl fluoride reactant) was vented from the reactor over a 3-hour period. The reactor was then resealed and water (6.0 kg) was added slowly to the reactor. After the exothermic reaction of the water with unreacted heptafluorobutyryl fluoride had subsided, the reactor was cooled to 25°C and the reactor contents were stirred for 30 minutes. The reactor pressure was carefully vented, and the lower organic phase was removed, affording 22.6 kg of material which was 63.2% by weight  $C_4F_9OCH_3$  (b.p. of 58-60°C, product identity confirmed by GC/MS and by  $^1H$  and  $^{19}F$  NMR).

**Preparation of Perfluorobutyl Ethyl Ether ( $C_4F_9OC_2H_5$ )** – a 20 gallon (3.8 L) Hastalloy C reactor, equipped with stirrer and a cooling system, was charged with 7.0 kg (120.3 mol) of spray-dried potassium fluoride. The reactor was sealed, and the pressure inside the reactor was reduced to less than 100 torr. 22.5 kg of anhydrous dimethyl formamide was then added to the reactor, and the reactor was cooled to below 0°C with constant agitation. 22.5 kg (60.6 mol) of heptafluorobutyryl fluoride (58% purity) was added to the reactor. When the temperature of the contents of the reactor reached -20°C, 18.6 kg (120.8 mol) of diethyl sulfate was added to the reactor over a period of approximately 2 hours. The resulting mixture was allowed to react for 16 hours with continuous agitation. The temperature was raised to 50°C for an additional 4 hours to facilitate complete reaction, and then the temperature was cooled to 20°C. After cooling, volatile material (primarily perfluorooxacyclopentane present in the starting heptafluorobutyryl fluoride reactant) was vented from the reactor over a 3-hour period. The reactor was resealed and water (6.0 kg) was added slowly to the

reactor. After the exothermic reaction of the water with unreacted heptafluorobutyl fluoride had subsided, the reactor was cooled to 25°C and the reactor contents were stirred for 30 minutes. The reactor pressure was carefully vented, and the lower organic phase was removed, affording 17.3 kg of material which was 73% by weight  $C_4F_9OCH_3$  (b.p. of 75°C, product identity confirmed by GC/MS and by  $^1H$  and  $^{19}F$  NMR).

**Preparation of Perfluoropropyl Methyl Ether ( $C_3F_7OCH_3$ )** – a jacketed 1-L round bottom flask was equipped with an overhead stirrer, a solid carbon dioxide/acetone condenser and an addition funnel. The flask was charged with 85 g (1.46 mol) of spray-dried potassium fluoride and 375 g of anhydrous diethylene glycol and was then cooled to about -20°C using a recirculating refrigeration system. 196 g (1.18 mol) of  $C_2F_5COF$  was added to the flask over a one hour period. The flask and its contents were warmed to about 24°C, and 184.3 g (1.46 mol) of dimethyl sulfate was added dropwise via the addition funnel over a 45 minute period. The resulting mixture was stirred overnight at room temperature. Water (a total of 318 mL) was added dropwise to the mixture. The mixture was transferred to a 1-L round bottom flask, and the resulting ether product was azeotropically distilled. The lower product phase of the resulting distillate was separated from the upper aqueous phase, was washed once with cold water, and was subsequently distilled to give 180 g of  $C_3F_7OCH_3$  product (b.p. 36°C, >99.9% purity by GLC). The product identity was confirmed by GCMS and by  $^1H$  and  $^{19}F$  NMR.

### **Example 1**

This example describes a laboratory scale dehydration of an aqueous solution of lithium bis(trifluoromethanesulfonyl) imide using perfluorobutyl methyl ether.

80 g of Fluorad™ HQ-115 Lithium Trifluoromethanesulfonimide (available from 3M Co., St. Paul, Minnesota) was dissolved in 20.5 g of distilled water. This solution and 120 g of  $C_4F_9OCH_3$  were placed in a 250 mL round bottom flask



equipped with a Dean-Stark distillation head, thermometer, condenser, heating mantle, magnetic stirrer, and stirring bar.

Temperature was adjusted to allow sufficient heat flow to give a reflux rate of about 10 L/min. The resulting  $C_4F_9OCH_3$ /water azeotrope was observed to boil at about 60°C, and the condensate was collected in the Dean-Stark trap. Water was separated from the condensate according to the elapsed time schedule shown in Table 1.

TABLE 1

Elapsed Time (hr)	Incremental Water Removed (g)	Total Water Removed (g)	General Comments
0.25	1	1	
0.5	1	2	
0.75	1	3	
1.0	1	4	
1.25	1	5	
1.5	1	6	
1.75	1	7	
2.0	0.4	7.4	
2.5	1.6	9	
3	0.7	9.7	
3.25	1	10.7	
3.5	0.6	11.3	
6.0	1	12.3	
7.5	0.6	12.9	water removal rate slowed considerably, 50 g of HFE added, reflux rate adjusted to 20 mL/min
7.8			apparent formation of solid
10.4	3.9	16.8	slurry formed, 41 g of HFE added to maintain stirring
11.8	2.4	19.2	20 g of HFE added to maintain stirring
12.7	0.9	20.1	free-flowing slurry observed, clear HFE layer in receiver (formerly cloudy)
13.4	0	20.1	distillation experiment terminated

After stopping the distillation experiment after 13.4 hours, the slurry of HFE/HQ-115 was vacuum filtered through a size C fritted glass filter, drawing nitrogen through the filter cake to dry the product. A free-flowing, iridescent

powder with plate-like crystal structure resulted. Through this process, 20.1 g of water (98% of the 20.4 g theoretical) was recovered.

### **Example 2**

5           This example describes a pilot scale dehydration of an aqueous solution of lithium bis(trifluoromethanesulfonyl)imide using perfluorobutyl methyl ether, and reports the results of a water analysis on the dehydrated imide salt.

10           1000 g of an 83% (wt) aqueous solution of HQ-115 and 2500 g of perfluorobutyl methyl ether were charged to a pilot scale reactor. The mixture was refluxed continually, returning to the distillation vessel the perfluorobutyl methyl ether captured in the trap. 183.2 g of water was recovered, representing nearly the theoretical amount for quantitative dehydration. The resulting white slurry of imide salt and the perfluorobutyl methyl ether was filtered in the -76°C dew point dry room, producing a white, free-flowing, iridescent powder. A 1M (1 molar) solution of this powder was prepared in propylene carbonate. Karl Fisher titrations run on 15 both the 1M solution (240 ppm) and propylene carbonate alone (175 ppm) showed that the dehydrated imide salt contained about 65 ppm residual moisture.

### **Example 3**

20           Essentially the same experiment was run as described in Example 1, except that 101 g of a 73% (wt) aqueous solution of lithium triflate (Fluorad™ FC-122 Lithium Trifluoromethanesulfonate, available from 3M Co.) and 200 g of perfluorobutyl methyl ether were used. The process proceeded in a similar fashion as was described in Example 1, with the recovery of 27.0 g of water, representing 25 an essentially quantitative removal of water.

### **Example 4**

30           Essentially the same experiment was run as described in Example 1, except that 10 g of a 82% (wt) aqueous solution of lithium bis(pentafluoroethanesulfonyl) imide (prepared as described in Example 3 of U.S. Pat. No. 5,652,072) and 200 g of perfluorobutyl methyl ether were used. The process proceeded in a similar

fashion as was described in Example 1, with the apparent quantitative removal of water. Analysis of the sample the sample purity to be 99.91% of the desired dehydrated imide salt, with traces of hydrofluoroethers as the only detectable-impurity.

5

### Example 5

This example describes a laboratory scale preparation and subsequent dehydration of an antistatic phosphonium triflate compound,  $(C_6H_5)_3(CH_3)P^+ O_3SCF_3$  (described in U.S. Pat. No. 5,051,330, Table 3, compound 10 2a), using perfluorobutyl methyl ether as the azeotroping solvent.

In a 3-necked flask equipped with stirrer, cooler, and condenser, and under a nitrogen blanket was charged 26.2 g (0.1 mol) of triphenylphosphine (available from Aldrich Chem. Co., Milwaukee, Wisconsin) and 400 mL of anhydrous diethyl ether. Then, at room temperature, 16.4 g (0.1 mol) of methyl 15 trifluoromethanesulfonate was added slowly over about a 30 minute time period. A white precipitate slowly formed while reacting for 24 hours at room temperature under nitrogen. The white precipitate was filtered, washed with deionized water, and filtered again, leaving a water-damp precipitate. 100 g of  $C_4F_9OCH_3$ , perfluorobutyl methyl ether, was added to the water-damp precipitate, and the 20 precipitate was dried by azeotropic distillation using a Dean-Stark trap. After no further water was coming over with the  $C_4F_9OCH_3$ , the  $C_4F_9OCH_3$  was evaporated off. A white solid resulted, which contained 40 ppm of water according to Karl-Fisher analysis.

### 25 Comparative Example C1

The same experiment was run in the same manner as described in Example 5, except that  $C_6F_{14}$ , perfluorohexane, was substituted for  $C_4F_9OCH_3$ . During the early stages of the azeotropic distillation step, foaming started to such an extent that the distillation could not be continued. The  $C_6F_{14}$  was then allowed to evaporate, 30 leaving a white solids which, through Karl Fisher analysis, was found to contain about 1000 ppm of water.

**Example 6**

This example describes a laboratory scale dehydration of an aqueous solution of lithium perfluorooctanesulfonate using perfluorobutyl methyl ether.

200 g fluorochemical surfactant (26% lithium perfluorooctanesulfonate in water) and 450 g of  $C_4F_9OCH_3$  were added to a 500 mL round-bottom flask equipped with a Dean-Stark distillation head, thermometer, condenser, heating mantle, magnetic stirrer, and stirring bar. Approximately 50 g of  $C_4F_9OCH_3$  was placed in the azeotrope receiver. The resulting mixture was heated, but too much foam was produced to boil off the  $C_4F_9OCH_3$ . Addition of up to 40 drops of isopropyl alcohol temporarily reduced foaming but only for a short duration.

To gain more reaction reactor space, the mixture was transferred to a 1-L round-bottom flask equipped the same way as the 500 mL flask. The flask and its contents were heated to boiling, and 100 mL of  $C_4F_9OCH_3$  was distilled through the Dean-Stark head. 100 mL of  $C_4F_9OCH_3$  was added back to the reaction, and the  $C_4F_9OCH_3$  was distilled off at a rate of about 10 ml/hour. After approximately 6 hours, the salt began phasing out of solution, forming large amounts of white, voluminous solid. Over time, the lumps gradually broke up into a powdery slurry. After about 16 hours of distillation time, less than 2 ml/hour of water was collecting in the Dean-Stark trap, so the distillation was stopped.

The resulting slurry was filtered through Whatman #1 filter paper, and the precipitate was oven dried to recover 52.6 g of a slightly off-white powder.

**Example 7**

Essentially the same laboratory scale dehydration experiment of lithium perfluorooctanesulfonate was run as described in Example 6 except that instead of pure  $C_4F_9OCH_3$ , an azeotropic solvent mixture consisting of a 50/50 (w/w)  $C_4F_9OCH_3$ /*trans*-dichloroethylene was used. Also, no solvent was initially placed in the receiver. The head temperature was maintained at 39°C.

After heating the mixture for about 5 hours, 4.8 g of water was collected in the Dean-Stark distillation head. 300 g more of the azeotropic solvent mixture was then added to the flask to reduce foaming. After an additional 2 hours, 6.0 mL of

water had been collected. The apparatus was shut down for the night, and next morning 200 mL more of the azeotropic solvent mixture was added. After 1 hour, the total collection of water had reached 10.1 g. After 6 hours from the morning restart, 200 mL more of the azeotropic solvent mixture was added. After 45 more  
5 minutes, the procedure was terminated for the day.

Next morning, a gel formed which was no longer stirrable. The flask and its contents were heated to reflux with stirring for an additional 8 hours. Over this time, the contents in the flask began turning white. The azeotroping was then stopped, and the contents of the flask were filtered to recover 47.4 g of slightly off-  
10 white powder (original FC-94 contained 52 g theoretical solids).

### Example 8

This example describes a laboratory scale dehydration of wet desiccant using perfluorobutyl methyl ether,  $C_4F_9OCH_3$ .

15 148.77 g of "the<sup>TM</sup>" desiccant (available from EMS Science, Gibbstown, N) was conditioned from the moisture of a wet sponge for a period of 3 days. The desiccant turned pink and became virtually wet, indicating a large amount of water absorption. The wet desiccant was then transferred to a round-bottom flask equipped with a Dean-Stark distillation head, thermometer, condenser, heating  
20 mantle, magnetic stirrer and stirring bar. To the flask was then added 928.7 g of perfluorobutyl methyl ether. The flask and its contents were heated to reflux with stirring. After ½ hour, 10.3 g of water was collected in the Dean-Stark distillation head, though the desiccant remained pink. After 1 hour, many blue desiccant  
25 spheres were evident, indicating the beginning of desiccant dehydration. After 2.75 hours, 26.8 g of water had been collected and the desiccant was bright blue, indicating a high level of dehydration. The flask and its contents were heated for an additional 8 hours, after which the total amount of collected water was 35.8 g.

### Example 9

30 In Example 9, essentially the same dehydration procedure was followed as described in Example 1 except that 100 g of a 75% (w/w) aqueous solution of FC-

122 (lithium triflate) was dehydrated using an azeotropic solvent consisting of 851 g of perfluoropropyl methyl ether ( $C_3F_7OCH_3$ ). The dehydration process was run at 34°C, the boiling point of the mixture. After 43 hours, 23.4 g of water (94% of the theoretical amount) had been captured by the Dean-Stark distillation head.

5

#### **Example 10**

In Example 10, essentially the same dehydration procedure was followed as described in Example 1, except that 100 g of a 75% (w/w) aqueous solution of FC-122 (lithium triflate) was dehydrated using an azeotropic solvent consisting of 825 g of perfluorobutyl ethyl ether ( $C_4F_9OC_2H_5$ ). The dehydration process was run at 77°C, the boiling point of the mixture. After 8.5 hours, 26.3 g of water (100% of the theoretical amount) had been captured by the Dean-Stark distillation head.

#### **Example 11**

In Example 11, essentially the same dehydration procedure was followed as described in Example 1, except that 135 g of a 75% (w/w) aqueous solution of lithium bis(perfluoroethylsulfonyl)imide (prepared using the procedure described in Example 3 of U.S. Pat. No. 5,652,072) was dehydrated using an azeotropic solvent consisting of 692 g of  $C_4F_9OC_2H_5$ . The dehydration process was run at 77°C, the boiling point of the mixture. After 5.5 hours, 33.7 g of water (100% of the theoretical amount) had been captured by the Dean-Stark distillation head.

#### **Example 12**

This example shows the dehydration of an electrolyte solution consisting of lithium triflate, water and propylene carbonate.

An electrolyte solution was made consisting of 75.4 g of FC-122 (lithium triflate), 25.2 g of deionized water and 75 g of 99% propylene carbonate (available from Aldrich Chemical Co., Milwaukee, WI). To a round-bottom flask equipped with a Dean-Stark distillation head, thermometer, condenser, heating mantle, magnetic stirrer, and stirring bar was added 625 g of  $C_4F_9OC_2H_5$  and the above-made electrolyte solution. The resulting mixture was heated to 77°C with stirring.

After 3.3 hours of heating time, 25.6 g of water (100% of theoretical) had collected in the distillation head, leaving in the flask a clear, colorless dehydrated electrolyte salt solution layer on top of a hydrofluoroether layer.

5 **Example 13**

This example shows the dehydration of an electrolyte solution consisting of lithium triflate and water using a non-ether hydrofluorocarbon.

The azeotrope process was run and completed as described in Example 1 except for the following modifications. 76.8 g of FC-122 (lithium triflate),  
10 previously dried in a vacuum oven, was dissolved in 26 g of distilled water. To this aqueous solution was added 825 g of Vertrel™ XF (CF<sub>3</sub>CFHCFHCF<sub>2</sub>CF<sub>3</sub>, having a boiling point of 55°C, available from E. I. duPont de Numours and Co.). The azeotrope process was run for a total of 8 hours, and the amount of water removed as a function of time is shown in TABLE 2.

15

**TABLE 2**

Elapsed Time (hr)	Incremental Water Removed (g)	Total Water Removed (g)	% of Theoretical Water Removed
1.0	6.3	6.3	24.2
2.0	4.2	10.5	40.4
3.0	4.7	15.2	58.5
5.5	7.8	23.0	88.5
7.0	2.4	25.4	97.7
8.0	0.4	25.8	99.2

The data in TABLE 2 show that, using the hydrofluorocarbon for azeotropic processing, over 99% of the water was removed after 8 hours.

Claims:

1. A method of dehydrating a hydrous substrate, the method comprising the steps of  
combining the hydrous substrate with a hydrofluorocarbon to form a  
5 hydrous hydrofluorocarbon composition, and  
volatilizing the hydrous hydrofluorocarbon composition to remove water.
2. The method of claim 1 wherein the hydrofluorocarbon contains  
10 substantially no surfactant.
3. The method of claim 1 wherein the hydrous hydrofluorocarbon composition contains substantially no surfactant.
- 15 4. The method of claim 1 wherein the hydrous hydrofluorocarbon composition consists essentially of surfactant, hydrofluorocarbon, water, and no added surfactant.
5. The method of claim 1 wherein the volatilization step includes the  
20 process of azeotropic distillation of the hydrous hydrofluorocarbon composition.
6. The method of claim 5 wherein the azeotropic distillation occurs at a temperature in the range from about 0C to about 100C.
- 25 7. The method of claim 1 wherein the substrate comprises a chemical composition chosen from the group consisting of a salt compound, a polar organic solvent, and mixtures thereof.
8. The method of claim 1 wherein the substrate comprises a fluorinated  
30 salt selected from the group consisting of lithium trifluoromethanesulfonate, lithium perfluorooctanesulfonate, barium trifluoromethanesulfonate, lithium



bis(trifluoromethanesulfonyl) imide, lithium bis(pentafluoroethanesulfonyl) imide, lithium(perfluorooctanesulfonyl)(trifluoromethanesulfonyl) imide, lithium (perfluorobutanesulfonyl)(trifluoromethanesulfonyl) imide, sodium bis(trifluoromethanesulfonyl) imide, lithium tris(trifluoromethanesulfonyl) methide,  
5 lithium hexafluorophosphate, lithium tetrafluoroborate, and lithium hydroxide monohydrate.

9. The method of claim 1 wherein the substrate comprises lithium trifluoromethanesulfonate, lithium bis(trifluoromethanesulfonyl) imide, or lithium  
10 bis(pentafluoroethanesulfonyl) imide.

10. The method of claim 9 wherein the substrate comprises a solution of lithium trifluoromethanesulfonate, lithium bis(trifluoromethanesulfonyl) imide or lithium bis(pentafluoroethanesulfonyl) imide, and an organic solvent.  
15

11. The method of claim 10 wherein the organic solvent comprises propylene carbonate.

12. The method of claim 1 wherein the water is volatilized from the  
20 hydrous hydrofluorocarbon composition to provide a dehydrated hydrofluorocarbon composition comprising substrate, hydrofluorocarbon, and a reduced amount of water.

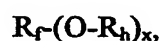
13. The method of claim 12 wherein the dehydrated hydrofluorocarbon  
25 composition contains less than about 100 parts water per million parts dehydrated hydrofluorocarbon composition.

14. The method of claim 1 further comprising the steps of  
collecting distillate from the volatilized hydrous hydrofluorocarbon  
30 composition, the distillate comprising hydrofluorocarbon and water,  
allowing the distillate to phase separate, and

returning hydrofluorocarbon to the hydrous hydrofluorocarbon composition.

15. The method of claim 1 wherein the hydrofluorocarbon comprises a hydrofluoroether.

16 The method of claim 15 wherein the hydrofluoroether comprises hydrofluoroether of formula I:



10 wherein:

x is from 1 to about 3,

$R_f$  a perfluorinated hydrocarbon group having a valency x, and containing from about 2 to 15 carbon atoms, optionally comprising a terminal  $F_3S-$  group;

each  $R_h$  is independently a linear or branched alkyl group having from 1 to about 8 carbon atoms, a cycloalkyl-containing alkyl group having from 4 to about 8 carbon atoms, or a cycloalkyl group having from about 3 to about 8 carbon atoms; wherein either or both of  $R_f$  and  $R_h$  can optionally contain one or more catenary heteroatoms;

wherein the sum of the number of carbon atoms in the  $R_f$  and  $R_h$  groups is preferably greater than or equal to 4.

17. The method of claim 16 wherein x is 1;  $R_f$  is a perfluoroalkyl comprising from about 3 to 10 carbons optionally containing one or more heteroatoms, and  $R_h$  is an alkyl group having from 1 to about 6 carbon atoms.

18. The method of claim 16 wherein the hydrofluoroether comprises a compound chosen from the group consisting of  $C_4F_9OCH_3$ ,  $C_4F_9OC_2H_5$ ,  $C_3F_7OCH_3$ , and mixtures thereof.

19. The method of claim 1 wherein the hydrofluorocarbon comprises  $CF_3CFHCFHCF_2CF_3$ .

20. A method of dehydrating a water-containing substrate comprising the steps of
- 5 providing a water-containing substrate comprising substrate and water, and
- adding hydrofluorocarbon to the water-containing substrate to provide a hydrous hydrofluorocarbon composition comprising substrate, water, and hydrofluorocarbon.
- 10 21. The method of claim 20 further comprising the step of removing water from the hydrous hydrofluorocarbon composition.
22. The method of claim 21 wherein water is removed mechanically from the hydrous hydrofluorocarbon composition.
- 15 23. The method of claim 21 wherein water is removed from the hydrous hydrofluorocarbon composition by volatilizing the hydrous hydrofluorocarbon composition.
- 20 24. The method of claim 23 wherein water is removed by azeotropic distillation.
- 25 25. The method of claim 20 wherein the water-containing substrate comprises a hydrous chemical salt optionally dispersed or dissolved in an organic solvent.
26. The method of claim 20 wherein the hydrofluorocarbon comprises a hydrofluoroether.
- 30 27. A method of dehydrating a hydrous substrate, the method comprising the steps of

providing a hydrous substrate comprising a fluorinated chemical salt and optionally an organic solvent,

combining the hydrous substrate with hydrofluoroether to form a hydrous hydrofluoroether composition,

5 azeotropically distilling the hydrous hydrofluoroether composition to volatilize water and the hydrofluoroether therein, to remove water from the hydrous hydrofluoroether composition and produce a dehydrated hydrofluoroether composition having a reduced water content;

10 optionally adding to the dehydrated hydrofluoroether composition a polar organic solvent; and

optionally separating the hydrofluoroether from the polar organic solvent.

28. The process of claim 27 wherein the substrate comprises a  
15 fluorinated salt chosen from the group consisting of lithium trifluoromethanesulfonate, lithium bis(trifluoromethanesulfonyl) imide, and lithium bis(pentafluoroethanesulfonyl) imide, and the optional polar organic solvent comprises propylene glycol.

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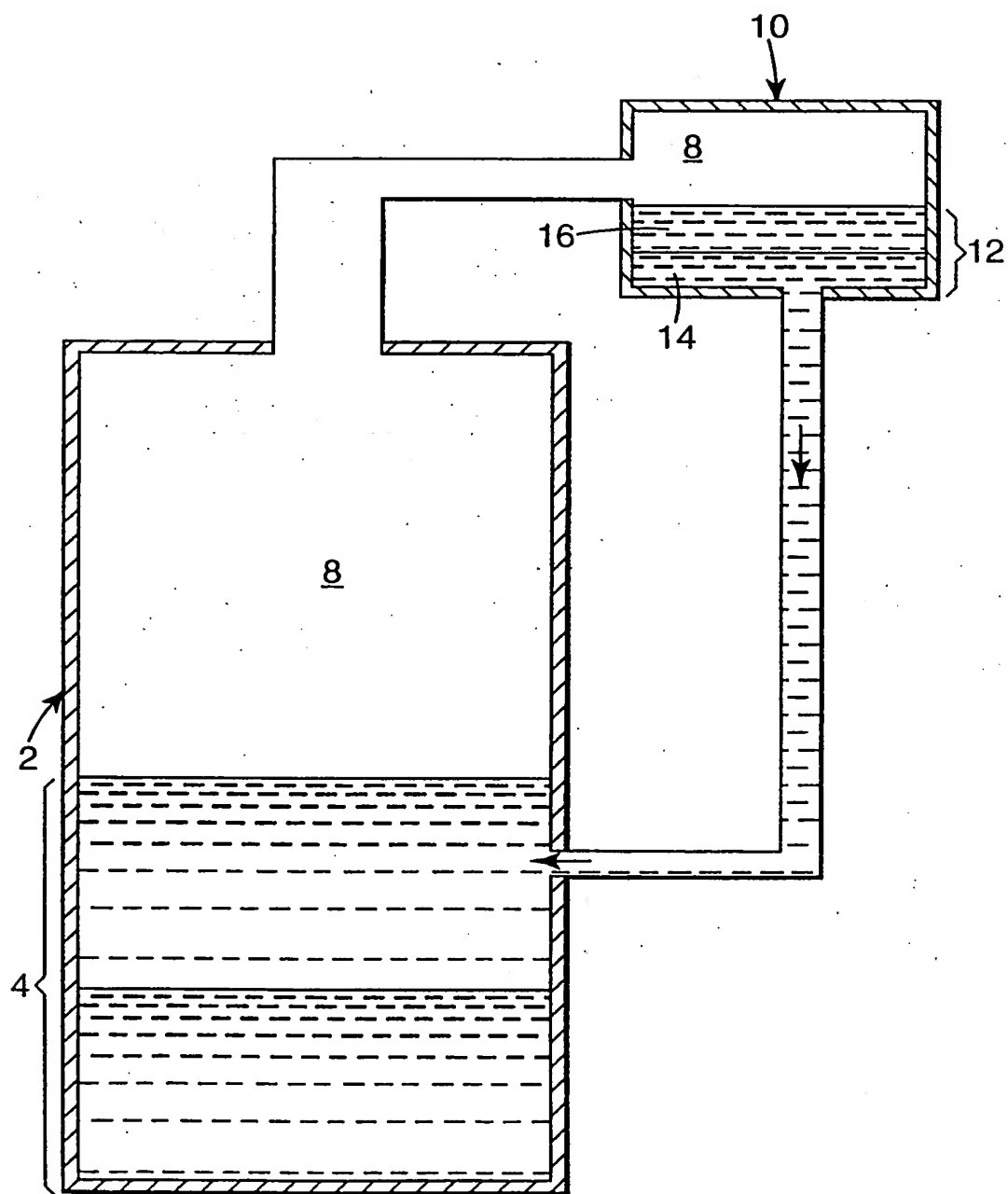


Fig. 1

# INTERNATIONAL SEARCH REPORT

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<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC 7    B01D12/00    F26B5/00    B01D17/025    B01D17/05				
According to International Patent Classification (IPC) or to both national classification and IPC				
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) IPC 7    B01D    F26B				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>				
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
X	PATENT ABSTRACTS OF JAPAN vol. 099, no. 002, 26 February 1999 (1999-02-26) & JP 10 290901 A (OTSUKA GIKEN KOGYO KK), 4 November 1998 (1998-11-04) abstract	1-3, 12, 14, 15, 20-23, 26		
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-/--				
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.				
<input checked="" type="checkbox"/> Patent family members are listed in annex.				
* Special categories of cited documents :				
<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; vertical-align: top; border: none;">           "A" document defining the general state of the art which is not considered to be of particular relevance            "E" earlier document but published on or after the international filing date            "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)            "O" document referring to an oral disclosure, use, exhibition or other means            "P" document published prior to the international filing date but later than the priority date claimed         </td> <td style="width: 50%; vertical-align: top; border: none;">           "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention            "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone            "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.            "&amp;" document member of the same patent family         </td> </tr> </table>			"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family			
Date of the actual completion of the international search  <div style="text-align: center;">3 September 1999</div>	Date of mailing of the international search report  <div style="text-align: center;">14/09/1999</div>			
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer  <div style="text-align: center;">De La Morinerie, B</div>			

# INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	EP 0 618 181 A (SOLVAY) 5 October 1994 (1994-10-05)  the whole document ----	1-3, 5, 6, 12-14, 20-24
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